

COMPOSITIONS, HALOGENATED COMPOSITIONS, CHEMICAL PRODUCTION AND TELOMERIZATION PROCESSES

CLAIM FOR PRIORITY

5 This application claims priority to United States Provisional Patent Application Serial Number 60/540,612, entitled Fluorine Functional Groups, Fluorine Compositions, Processes for Manufacturing Fluorine Compositions, and Material Treatments, filed January 30th, 2004, the entirety of which is incorporated by reference herein.

10 TECHNICAL FIELD

The disclosure pertains to compositions, halogenated compositions, chemical production and telomerization processes.

BACKGROUND

15 Compositions such as surfactants, polymers, and urethanes have incorporated halogenated functional groups. These functional groups have been incorporated to affect the performance of the composition when the composition is used as a treatment for materials and when the composition is used to enhance the performance of materials. For example, surfactants
20 incorporating halogenated functional groups can be used as fire extinguishants either alone or in formulations such as aqueous film forming foams (AFFF). Polymers and/or urethanes incorporating halogenated functional groups have also been used to treat materials. To prepare these compositions, halogenated intermediate compositions can be synthesized.

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SUMMARY

 Compositions are provided that can include $R_F(R_T)_nQ$ and/or one or both of $R_F(R_1-\underset{\underset{CF_3}{|}}{CH})_nQ$ and $Q(R_1-\underset{\underset{CF_3}{|}}{CH})_nR_F$. Within these compositions the R_F group can have at least four fluorine atoms, the R_T group can include at least one C-2
30 group having at least one pendant $-CF_3$ group, n can be at least 1, the R_1 group can include at least one carbon atom, and the Q group can include one or more atoms of the periodic table of elements. Compositions are provided that can also include $R_{Cl}(R_T)_nH$, with the R_{Cl} group having at least one $-CCl_3$ group.

 Telomerization processes are also provided that include exposing at least
35 one CF_3 -comprising taxogen to a fluorine-comprising telogen to produce a

telomer, with the fluorine-comprising telogen including at least four fluorine atoms.

BRIEF DESCRIPTION OF THE DRAWING

5 The Figure is a diagram of a system according to an exemplary embodiment of an exemplary aspect of the invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

10 This disclosure of the invention is submitted in furtherance of the constitutional purposes of the U.S. Patent Laws "to promote the progress of science and useful arts" (Article 1, Section 8).

 Compositions and methods of making compositions are described with reference to the Figure. Referring to the Figure, a system 10 is shown for preparing halogenated compositions that includes reagents such as a taxogen
15 2, a telogen 4, and an initiator 6 being provided to reactor 8 to form a product such as a telomer 9. In exemplary embodiments system 10 can perform a telomerization process. According to an embodiment, taxogen 2 can be exposed to telogen 4 to form telomer 9. In accordance with another
20 embodiment, taxogen 2 can be exposed to telogen 4 in the presence of initiator 6. Reactor 8 can also be configured to provide heat to the reagents during the exposing.

 Taxogen 2 can include at least one CF_3 -comprising compound. The CF_3 -comprising compound can have a C-2 group having at least one pendant $-\text{CF}_3$ group. In exemplary embodiments taxogen 2 can comprise an olefin, such as
25 3,3,3-trifluoropropene (TFP, trifluoropropene).

 Telogen 4 can include halogens such as fluorine and/or chlorine. Telogen 4 can include at least four fluorine atoms and can be represented as $\text{R}_\text{F}\text{Q}$ and/or $\text{R}_\text{Cl}\text{Q}$. The R_F group can include at least four fluorine atoms and the Q group can include one or more atoms of the periodic table of elements. The
30 Q group can be H or I with the R_F group being $(\text{CF}_3)_2\text{CF}-$ and/or $-\text{C}_6\text{F}_{13}$, for example. The R_Cl group can include at least one $-\text{CCl}_3$ group. Exemplary telogens can include $(\text{CF}_3)_2\text{CFI}$, $\text{C}_6\text{F}_{13}\text{I}$, trichloromethane, $\text{HP}(\text{O})(\text{OEt})_2$, $\text{BrCFClCF}_2\text{Br}$, R-SH (R being a group having carbon), and/or MeOH . In exemplary embodiments, taxogen 2 can include trifluoropropene and telogen 4
35 can include $(\text{CF}_3)_2\text{CFI}$, with a mole ratio of taxogen 2 to telogen 4 being from about 1:1 to about 1:10, 1:4 to about 4:1, and/or to about 2:1 to about 4:1.

Reactor 8 can be any lab-scale or industrial-scale reactor and, in certain embodiments, reactor 8 can be configured to control the temperature of the reagents therein. According to exemplary embodiments reactor 8 can be used to provide a temperature during the exposing of the reagents of from about 130°C to about 150°C.

Telomer 9, produced upon exposing taxogen 2 to telogen 4, can include $R_F(R_T)_nQ$ and/or $R_{Cl}(R_T)_nH$. The R_T group can include at least one C-2 group

having a pendant $-CF_3$ group, such as $-CH_2-\underset{\substack{| \\ CF_3}}{CH}-$. Exemplary products include $Q(R_1-\underset{\substack{| \\ CF_3}}{CH})_nR_F$, $R_F(R_1-\underset{\substack{| \\ CF_3}}{CH})Q$, $R_F(R_1-\underset{\substack{| \\ CF_3}}{CH})_nQ$ and $R_F(CH_2-\underset{\substack{| \\ CF_3}}{CH})_nQ$, with R_1 including at least one carbon atom, such as $-CH_2-$, for

example. In exemplary embodiments, n can be at least 1 and in other embodiments n can be at least 2 and the product can include one or more of

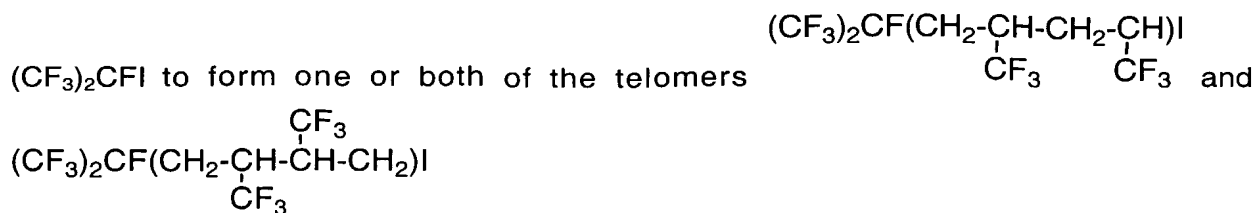
$R_F(CH_2-\underset{\substack{| \\ CF_3}}{CH}-CH_2-\underset{\substack{| \\ CF_3}}{CH})Q$, $R_F(CH_2-\underset{\substack{| \\ CF_3}}{CH}-\underset{\substack{| \\ CF_3}}{CH}-CH_2)Q$, $R_{Cl}(CH_2-\underset{\substack{| \\ CF_3}}{CH}-CH_2-\underset{\substack{| \\ CF_3}}{CH})H$ and/or $R_{Cl}(CH_2-\underset{\substack{| \\ CF_3}}{CH}-\underset{\substack{| \\ CF_3}}{CH}-CH_2)H$.

In an exemplary embodiment, the taxogen trifluoropropene can be exposed to the telogen $(CF_3)_2CFI$ to form the telomer $(CF_3)_2CF(CH_2-\underset{\substack{| \\ CF_3}}{CH})_nI$, and,

by way of another example, trifluoropropene can be exposed to the telogen $C_6F_{13}I$ to form the telomer $C_6F_{13}(CH_2-\underset{\substack{| \\ CF_3}}{CH})_nI$. In accordance with another

embodiment, the taxogen trifluoropropene can also be exposed to the telogen $CCl_3(CH_2-\underset{\substack{| \\ CF_3}}{CH})_nZ$, ($Z=H$, Br , and/or Cl , for example) to form the telomer $CCl_3(CH_2-\underset{\substack{| \\ CF_3}}{CH})_nZ$.

Products having n being at least 2 can be formed when utilizing an excess of the taxogen as compared to the telogen. For example, at least a 2:1 mole ratio of the taxogen to the telogen can be utilized to obtain products having n being at least 2. For example and by way of example only, at least two moles of the taxogen trifluoropropene can be exposed to at least one mole of the telogen



In additional embodiments initiator 6 may be provided to reactor 8 during the exposing of the reagents. Initiator 6 can include thermal, photochemical (UV), radical, and/or metal complexes, for example, including a peroxide such as di-tert-butyl peroxide. Initiator 6 can also include catalysts, such as Cu. Initiator 6 and telogen 4 can be provided to reactor 8 at a mole ratio of initiator 6 to taxogen 2 of from between about 0.001 to about 0.05 and/or from between about 0.01 to about 0.03, for example.

According to exemplary embodiments, various initiators 6 and telogens 4 can be used to telomerize taxogen 2 as referenced in Table 1 below. Telomerizations utilizing photochemical and/or metal-complex initiators 6 can be carried out in batch conditions using Carius tube reactors 8. Telomerizations utilizing thermal and/or peroxide initiators 6 can be carried out in 160 and/or 500 cm³ Hastelloy reactors 8. Telogen 4 (neat and/or as a peroxide solution) can be provided as a gas at a temperature from about 60 °C to about 180 °C and a telogen 4 [T]₀ /taxogen 2 [Tx]₀ initial molar ratio R₀ can be varied from 0.25 to 1.5 and the reaction time from 4 to 24 hrs as dictated in Table 1 below. The product mixture can be analyzed by gas chromatography and/or the product can be distilled into different fractions and analyzed by ¹H and ¹⁹F NMR and/or ¹³C NMR. MonoAdduct (n=1) and DiAdduct (n=2) products can be recognized as shown in Table 1 below.

Table 1. Telomerization of Trifluoropropene Taxogen

| Run ^a | Init. ^d | R ₀ ^b | C ₀ ^b | T (°C) | t _r (hrs) | P (bars) | | % Conv. of Taxogen | Yield (%) by GC ^c | | |
|------------------|--------------------|-----------------------------|-----------------------------|--------|----------------------|----------|-----|--------------------|------------------------------|------------------|----------------|
| | | | | | | | | | Telogen | MonoAdduct (n=1) | DiAdduct (n=2) |
| 1 | Therm | 0.50 | - | 160 | 20 | 22 | 17 | 79.2 | 27.6 | 51.9 | 20.5 |
| 2 | Therm | 0.25 | - | 160 | 20 | 39 | 34 | 36.8 | 52.8 | 26.2 | 21 |
| 3 | Therm | 0.50 | - | 180 | 22 | 30 | 11 | 73.4 | 2.4 | 65.9 | 31.2 |
| 4 | Perk | 0.50 | 0.03 | 62 | 20 | 7 | 5 | 79.2 | 23.8 | 35.4 | 40.8 |
| 5 | AIBN | 0.50 | 0.03 | 82 | 18 | 10 | 7 | 79.2 | 17.4 | 38.8 | 42 |
| 6 | TRIG | 0.50 | 0.03 | 134 | 6 | 16 | 0.6 | 89.6 | 3.7 | 19 | 63.8 |
| 7 | DTBP | 0.50 | 0.03 | 140 | 6 | 17 | 0.2 | 97.9 | 3.7 | 19 | 63.8 |
| 8 | DTBP | 0.50 | 0.03 | 143 | 4 | 19 | 0.8 | 94.3 | 9.6 | 21 | 66.6 |
| 9 | DTBP | 1.4 | 0.03 | 150 | 4 | 13 | 1.1 | 95.2 | 22.5 | 54.4 | 15.7 |
| 10 | DTBP | 0.75 | 0.03 | 145 | 4 | 20 | 3.0 | 93.8 | 6.8 | 34.1 | 49.0 |
| 11 | DTBP | 1.2 | 0.03 | 150 | 4 | 20 | 5.0 | 90.0 | 14.9 | 46.3 | 33.4 |
| 12 | DTBP | 1.4 | 0.03 | 150 | 4 | 21 | 3.5 | 95.0 | 12.6 | 54.1 | 28.6 |
| 13 | DTBP | 1.5 | 0.03 | 150 | 4 | 19 | 5.0 | 95.0 | 24.6 | 43.9 | 28.3 |

a) Telogen can be C₆F₁₃l in Runs Nos 1-9 and (CF₃)₂CFI in Runs No 10-13

b) $R_0 = [I]_0/[Tx]_0$; $C_0 = [In]_0/[Tx]$

c) Heavy TFP telomers (n>2) can make up remainder of product

d) Initiators can be Perk. 16s(t-butyl cyclohexyl dicarbonate); AIBN; Trig.101 (2,5-bis-(t-butyl peroxy)-2,5-dimethylhexane); and DTBP.